DESCRIPTION

Carbon Material for Battery Electrode and Production Method and Use Thereof

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CROSS-REFERENCE TO RELATED APPLICATIONS

This is an application filed pursuant to 35 U.S.C. Section 111(a) with claiming the benefit of U.S. provisional application Serial No. 60/518,660 filed November 12, 2003

10   under the provision of 35 U.S.C. 111(b), pursuant to 35 U.S.C. Section 119(e)(1).

TECHNICAL FIELD

The present invention relates to an electrode material

15   for a battery, particularly for a non-aqueous electrolytic solution secondary battery, having a high charge/discharge capacity and exhibiting excellent charge/discharge cycle characteristics and large-current load characteristics, to an electrode employing the material, and to a non-aqueous

20   electrolytic solution secondary battery employing the material. More particularly, the invention relates to a negative electrode material for a lithium secondary battery, to a negative electrode employing the negative electrode material, and to a lithium secondary battery employing the

25   negative electrode material.

BACKGROUND ART

In accordance with development of small-sized, lightweight portable electronic apparatuses of high

30   performance, keen demand has arisen for a lithium ion secondary battery having high energy density; i.e., high

capacity. In most lithium ion secondary batteries, graphite fine powder is employed as a negative electrode material, since lithium ions can intercalate between layers of graphite. The more crystalline the graphite, the higher

5 discharge capacity the graphite exhibits. Therefore, studies have been made on use of high-crystallinity carbon materials as a negative electrode material, *inter alia*, natural graphite as the most preferable, for a lithium ion secondary battery. When employed in a negative electrode, a graphite

10 material theoretically exhibits a discharge capacity of 372 mAh/g. However, improvement of such graphite material has proceeded, and in recent years, graphite material having a discharge capacity within a practical range of 350 to 360 mAh/g has been developed.

15   As mentioned above, the discharge capacity per weight has been improved to a level nearly equal to a theoretical value. Thus, the recent trend is toward elevating density of battery electrodes by high compression molding, so that the discharge capacity per volume can be enhanced through

20 increasing the filling density of electrode material charged in a battery housing.

     As the crystallinity of graphite increases, there arise problems of decrease in coulombic efficiency (i.e., initial discharge capacity/initial charge capacity) and increase in

25 irreversible capacity, which are conceivably caused by decomposition of an electrolyte (see J. Electrochem. Soc., Vol. 117, 1970, p. 222). Thus, in an attempt to solve the above problems, there has been proposed a negative electrode material in which a high-crystallinity carbon material member

30 is coated with amorphous carbon, so as to suppress decrease in coulombic efficiency and increase in irreversible capacity,

2

which are conceivably caused by decomposition of an
electrolyte, as well as deterioration of cycle
characteristics (see EP No.520667 and JP-A-11-310405).
However, the technique disclosed in EP No.520667 where an

5   amorphous carbon layer is formed on a high-crystallinity
carbon material member through CVD (chemical vapor deposition,
or vapor phase deposition) involves serious practical
problems of high cost, low mass productivity and the like.
In addition, a negative electrode material coated with an

10   amorphous carbon layer, a so-called double-layer carbon
material, still has drawbacks stemming from the amorphous
carbon layer; e.g., low capacity and low coulombic efficiency.
Although JP-A-11-310405 and other documents disclose a
technique in which an amorphous carbon layer is formed

15   through a liquid-phase carbon formation method, which is
advantageous in terms of cost and mass productivity, the
aforementioned drawbacks involved in the amorphous carbon
layer have not yet been resolved.

     Particles of high-crystallinity graphite (e.g., natural

20   graphite) tend to be deformed through application of pressure,
and the layer structure of the graphite tends to be oriented.
Such deformation/orientation occurs during fabrication of an
electrode (i.e., application of paste or pressing), thereby
raising problems; falling of the fabricated electrode, poor

25   impregnation performance with respect to electrolyte, and
deterioration of current-load characteristics and cycle
characteristics. These problems have not been solved
completely even in the aforementioned techniques where the
carbon member is coated with an amorphous carbon layer.

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DISCLOSURE OF THE INVENTION

Thus, an object of the present invention is to prepare
carbon particles having a particle size of several tens of nm
to several hundreds of μm, each particle having a virtually
homogeneous structure from the surface to the center of the
5   particle by compounding and integrating a carbonaceous
particle (particularly natural graphite particles) serving as
a core material with other carbon materials, and thereby
provide a battery electrode material which undergoes less
deformation/orientation due to application of pressure, has a
10 large discharge capacity, exhibits excellent coulombic
efficiency and cycle characteristics, is employable under
large current conditions, and has small irreversible capacity.

The present inventors have carried out extensive studies
in order to solve the aforementioned problems involved in the
15 related art, and have found that carbon particles, each
particle having a virtually homogeneous structure from the
surface to the center thereof, can be produced by uniformly
incorporating a specific amount of an organic substance into
high-crystallinity graphite particles having a specific
20 particle size, through impregnation or compounding, and by
carbonizing the organic substance at high temperature, and
that when the ratio of peak intensity attributed to a (110)
plane to that attributed to a (004) plane, the ratio being
determined through X-ray diffraction spectroscopic analysis
25 of a specific press-molded compact containing the carbon
particles, reaches a specific value (≥0.1), a battery
electrode material which undergoes less pressure-induced
deformation, exhibits low shape selectivity of particles
(after pressure has been applied thereto), exhibits excellent
30 coulombic efficiency, cycle characteristics, large-current
characteristics, and has small irreversible capacity can be

produced without impairing a characteristically high discharge capacity of high-crystallinity graphite particles. The present invention has been accomplished on the basis of these findings.

5   Accordingly, the present invention is directed to the following carbon materials for battery electrodes, method for producing the carbon material, and use thereof.

[1] A carbon material for a battery electrode, which comprises a carbon powder material as a composite of

10   carbonaceous particles and an a carbon material derived from an organic compound prepared by allowing the organic compound serving as a polymer source material to deposit onto and/or permeate into the carbonaceous particles to thereby polymerize the polymer source material and then heating at

15   1,800 to 3,300°C, and which has an intensity ratio of 0.1 or more for peak intensity attributed to a (110) plane to peak intensity attributed to a (004) plane determined through X-ray diffraction spectroscopic analysis on a mixture of the carbon material and a binder resin when pressed at 10^3 kg/cm^2

20   or higher.

[2] The carbon material for a battery electrode as described in [1] above, wherein the carbonaceous particles are composed of natural graphite, petroleum-derived pitch coke or coal-derived pitch coke.

25   [3] The carbon material for a battery electrode as described in [1] or [2] above, wherein the carbonaceous particles are composed of high-crystallinity natural graphite which has the C_0 value of a (002) plane as determined through X-ray diffraction spectroscopy of 0.6703 to 0.6800 nm, La

30   (crystallite size in the a-axis direction) of greater than 100 nm (La > 100 nm) and Lc (crystallite size in the c-axis

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direction) of greater than 100 nm (Lc > 100 nm).

[4] The carbon material for a battery electrode as described in any one of [1] to [3] above, wherein the carbonaceous particles have a laser diffraction mean particle size of 10 to 40 μm.

[5] The carbon material for a battery electrode as described in any one of [1] to [4] above, wherein a mean roundness of the carbonaceous particles as measured by use of a flow particle image analyzer is 0.85 to 0.99.

[6] The carbon material for a battery electrode as described in any one of [1] to [5] above, wherein the laser Raman R value of the carbonaceous particles (the ratio of a peak intensity at 1,360 cm^{-1} to a peak intensity at 1,580 cm^{-1} in the laser Raman spectrum) is 0.01 to 0.9.

[7] The carbon material for a battery electrode as described in any one of [1] to [6] above, wherein the area ratio of a region including a diffraction pattern having two or more spots to a region including only one spot attributed to a (002) plane is 95 to 50 : 5 to 50 in a 5 μm square region arbitrarily selected from a transmission electron microscope bright field image of a cross-section surface obtained by cutting the carbonaceous particles into flake form.

[8] The carbon material for a battery electrode as described in any one of [1] to [7] above, wherein the carbon material derived from an organic compound is a graphitized material.

[9] The carbon material for a battery electrode as described in any one of [1] to [8] above, wherein the carbon material derived from an organic compound is contained in an amount of 2 to 200 parts by mass based on 100 parts by mass

6

of carbonaceous particles serving as a core material.

[10] The carbon material for a battery electrode as described in any one of [1] to [9] above, wherein graphite crystalline structure regions and amorphous structure regions are dispersed from the surface to the center in each of the particles constituting the carbon material.

[11] The carbon material for a battery electrode as described in any one of [1] to [10] above, wherein the area ratio of a region including a diffraction pattern having two or more spots to a region including only one spot attributed to a (002) plane is 99 to 30 : 1 to 70 in a 5 μm square region arbitrarily selected from a transmission electron microscope bright field image of a cross-section surface obtained by cutting the carbon material for a battery electrode into flake form.

[12] The carbon material for a battery electrode as described in any one of [1] to [11] above, which contains boron in an amount of 10 ppm to 5,000 ppm.

[13] The carbon material for a battery electrode as described in any one of [1] to [12] above, which contains carbon fiber having a fiber diameter of 2 to 1,000 nm.

[14] The carbon material for a battery electrode as described in [13] above, wherein at least portion of the carbon fiber is deposited on a surface of the carbon powder material.

[15] The carbon material for a battery electrode as described in [13] or [14] above, which contains carbon fiber in an amount of 0.01 to 20 parts by mass based on 100 parts by mass of the carbon powder material.

[16] The carbon material for a battery electrode as described in any one of [13] to [15] above, wherein the

7

carbon fiber is a vapor grown carbon fiber having an aspect ratio of 10 to 15,000.

[17] The carbon material for a battery electrode as described in [16] above, wherein the vapor grown carbon fiber is a graphite carbon fiber which has undergone heat treatment at 2,000°C or higher.

[18] The carbon material for a battery electrode as described in [16] or [17] above, wherein the vapor grown carbon fiber has, in its interior, a hollow structure.

[19] The carbon material for a battery electrode as described in any one of [16] to [18] above, wherein the vapor grown carbon fiber contains a branched carbon fiber.

[20] The carbon material for a battery electrode as described in any one of [16] to [19] above, wherein the vapor grown carbon fiber has a mean interlayer spacing (d_{002}) of a (002) plane of 0.344 nm or less as measured by means of X-ray diffractometry.

[21] The carbon material for a battery electrode as described in any one of [1] to [20] above, wherein the carbon powder material satisfies at least one of the following requirements:

(1) mean roundness as measured by use of a flow particle image analyzer is 0.85 to 0.99;

(2) C_0 value of a (002) plane as measured by means of X-ray diffractometry is 0.6703 to 0.6800 nm, La (crystallite size in the a-axis direction) is greater than 100 nm (La > 100 nm), and Lc (crystallite size in the c-axis direction) is greater than 100 nm (Lc > 100nm);

(3) BET specific surface area is 0.2 to 5 m^2/g;

(4) true density is 2.21 to 2.23 g/cm^3;

(5) laser Raman R value (the ratio of a peak intensity at

1,360 cm^{-1} in a laser Raman spectrum to a peak intensity at
1,580 cm^{-1} in the spectrum) is 0.01 to 0.9; and

(6) mean particle size as measured through laser
diffractometry is 10 to 40 μm.

5   [22] The carbon material for a battery electrode as
described in any one of [1] to [21] above, which has an
initial discharge capacity of 340 mAh/g or higher.

        [23] A method for producing a carbon material for a
battery electrode which is a carbon powder material as a

10   composite of carbonaceous particles and an a carbon material
derived from an organic compound and has an intensity ratio
of 0.1 or more for peak intensity attributed to a (110) plane
to peak intensity attributed to a (004) plane determined
through X-ray diffraction spectroscopic analysis on a mixture

15   of the carbon material and a binder resin when pressed at 10^3
kg/cm^2 or higher, comprising a step of allowing the organic
compound or a solution thereof serving as a polymer source
material to deposit onto and/or permeate into the
carbonaceous particles, a step of polymerizing the organic

20   compound and a step of heating the obtained particles at
1,800 to 3,300°C to thereby graphitize and/or carbonize the
particles.

        [24] The method for producing a carbon material for a
battery electrode as described in [23] above, wherein the

25   step of polymerizing the organic compound includes heat
treatment at 100 to 500°C, and the step of carbonizing and/or
graphitizing the particles includes heat treatment at 2,300°C
to 3,300°C.

        [25] The method for producing a carbon material for a

30   battery electrode as described in [23] or [24] above, wherein
the carbonaceous particles are natural graphite particles.

[26] A method for producing a carbon material for a battery electrode which is a carbon powder material as a composite of carbonaceous particles and an a carbon material derived from an organic compound and carbon fiber having a

5   filament diameter of 2 to 1000 nm with at least portion of the carbon fiber depositing on the carbonaceous particles and has an intensity ratio of 0.1 or more for peak intensity attributed to a (110) plane to peak intensity attributed to a (004) plane determined through X-ray diffraction

10   spectroscopic analysis on a mixture of the carbon material and a binder resin when pressed at 10^3 kg/cm^2 or higher, comprising a step of treating carbonaceous particles with a mixture or solution containing the organic compound serving as a polymer source material and carbon fiber having a

15   filament diameter of 2 to 1000 nm to thereby allow the organic compound to deposit onto and/or permeate into the carbonaceous particles and allow the carbon fiber to deposit onto the particles, a step of polymerizing the organic compound and a step of heating the obtained particles at

20   1,800 to 3,300°C.

[27] A carbon material for a battery electrode, which is produced through a method for producing a carbon material for a battery electrode as recited any of [23] to [26] above.

[28] A paste for producing an electrode, which comprises

25   a carbon material for a battery electrode as recited any one of [1] to [22] and [27] above, and a binder.

[29] An electrode formed of a compact of a paste as recited in [28] above.

[30] The electrode as described in [29] above, wherein

30   the ratio of peak intensity attributed to a (110) plane to that attributed to a (004) plane is 0.1 or more as determined

through X-ray diffraction spectroscopic analysis on the compact.

[31] A battery comprising as a constituent an electrode as recited in [29] or [30] above.

5   [32] A secondary battery comprising as a constituent an electrode as recited in [29] or [30] above.

[33] A secondary battery as described in [32], wherein the battery employs a non-aqueous electrolytic solution and/or a non-aqueous polymer electrolyte, and the non-aqueous

10   electrolytic solution and/or the non-aqueous polymer electrolyte contains a non-aqueous solvent which is at least one species selected from the group consisting of ethylene carbonate, diethyl carbonate, dimethyl carbonate, methyl ethyl carbonate, propylene carbonate, butylene carbonate, and

15   vinylene carbonate.

[34] A method for evaluating a carbon material for a battery electrode containing a composite carbon powder material of carbonaceous particles and an carbon material derived from an organic compound which is produced by

20   allowing the organic compound serving as a polymer source material to deposit onto and/or permeate into to carbonaceous particles serving as a core material, thereby polymerizing the organic compound, and then calcining the obtained particles at 1,800 to 3,300°C, wherein the

25   evaluation employs as an index, a ratio (0.1) of peak intensity attributed to a (110) plane to that attributed to a (004) plane determined through X-ray diffraction spectroscopic analysis on a mixture of the carbon material and a binder resin when pressed at 10^3 kg/cm^2 or higher.

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BRIEF DESCRIPTION OF DRAWINGS

Fig.1 is a chart showing an X-ray diffraction profile of the (004) plane of an electrode sheet fabricated from the carbonaceous powder of Example 2.

Fig.2 is a chart showing an X-ray diffraction profile of the (110) plane of an electrode sheet fabricated from the carbonaceous powder of Example 2.

Fig.3 is a chart showing an X-ray diffraction profile of the (004) plane of an electrode sheet fabricated from the carbonaceous powder of Comparative Example 1.

Fig.4 is a chart showing an X-ray diffraction profile of the (110) plane of an electrode sheet fabricated from the carbonaceous powder of Comparative Example 1.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will next be described in detail.

[Carbonaceous particles]

In the present invention, no particular limitation is imposed on the type of carbonaceous particles serving as a core material, so long as the particles allow intercalation and release of lithium ions. The larger the amount of lithium ions intercalated in and released from the carbonaceous particles, the more preferable. From the viewpoint, high-crystallinity graphite such as natural graphite is preferred. Such high-crystallinity graphite preferably has the following properties: C_0 of a (002) plane as measured by means of X-ray diffractometry is 0.6703 to 0.6800 nm; La (the size of a crystallite as measured along the a-axis) is greater than 100 nm; Lc (the size of a crystallite as measured along the c-axis) is greater than 100 nm; and laser Raman R value (the ratio of the intensity of a peak at 1,360 cm^{-1} in a laser Raman spectrum to that of a peak

12

at 1,580 cm^{-1} in the spectrum) is 0.01 to 0.9.

Alternatively, carbonaceous particles formed of easily-graphitizing carbon material (soft carbon), which is readily graphitized through heat treatment at 1,800 to 3,300°C

5   performed in a subsequent step, may also be employed. Examples of the carbon material include particles of a coke such as petroleum-derived pitch coke or coal-derived pitch coke.

The graphite particles which are preferably employed as

10   a core material in the present invention may have a shape of clods, flakes, spheres, fiber or the like. Among them, spherical graphite particles and clod-shape graphite particles are preferred. The graphite particles serving as a core material preferably have a mean roundness as measured by

15   use of a flow particle image analyzer of 0.85 to 0.99. When the mean roundness is less than 0.85, the density of graphite particles charged during formation of an electrode cannot be elevated, thereby lowering the discharge capacity per volume, whereas when the mean roundness is in excess of 0.99, it

20   means that the graphite particles contains virtually no microparticles having low roundness, thereby failing to elevate the discharge capacity during formation of an electrode. Furthermore, the amount of graphite particles having a roundness less than 0.90 is preferably controlled to

25   be within a range of 2 to 20% by number. The mean roundness may be regulated by use of, for example, a particle shape regulator (e.g., mechano-fusion (surface fusion) treatment).

The carbonaceous particles preferably have a mean particle size of 10 to 40 μm as determined through a laser

30   diffraction scattering method, more preferably 10 to 30 μm. The particle size distribution profile preferably includes

13

virtually no portions corresponding to particles having a particle size of 1 μm or less or of 80 μm or more. This is because when the particle size is excessively large, carbon powder contained in the carbon material for an electrode has

5   a large particle size. When such an electrode is employed as a negative electrode material for a secondary battery, microparticles are formed through charge/discharge reaction, thereby deteriorating cycle characteristics. When the particle size is too small, such carbonaceous particles do

10   not effectively involved in electrochemical reaction with lithium ions, thereby deteriorating capacity and cycle characteristics.

The particle size distribution may be regulated through a known method such as pulverization or classification.

15   Examples of pulverizing apparatuses include a hammer mill, a jaw crusher, and a collision-type pulverizer. Examples of classification methods employable in the invention include gas-flow classification and classification by means of a sieve. Examples of gas-flow classification apparatuses

20   include a Turbo Classifier and a Turboplex (Product names: manufactured by HOSOKAWA MICRON CORPORATION.).

The carbonaceous particles may assume a crystalline (graphite crystalline) carbon portion and an amorphous carbon portion, as observed in a bright field image under a

25   transmission electron microscope. The transmission electron microscope has long been employed in structural analysis of carbon materials. Among techniques by use of the microscope, a high-resolution technique, which realizes observation of a crystal plane as a lattice image, particularly a hexagonal

30   network plane as a (002) lattice image, enables direct observation of a layer structure of carbon at a magnification

14

of about 400,000 times or more. Thus, the transmission
electron microscope serves as a powerful tool for the
characterization of carbon, and is employed for analysis of a
crystalline carbon portion and an amorphous carbon portion.

5   Briefly, a region of interest in a bright field is
characterized on the basis of patterns obtained through
selected area electron diffraction (SAD). The
characterization is described in detail in "Novel
Experimental Techniques for Carbon Materials (analysis),"
10   edited by The Carbon Society of Japan, published by SIPEC
CORP., p. 18-26 and 44-50, and "Guide to Carbon material,
revised edition, authored by Michio Inagaki et al., edited by
The Carbon Society of Japan, p. 29-40.

        The term "crystalline region" used herein means a region
15   characterized by a diffraction pattern of, for example, a
readily-graphitizing carbon treated at 2,800°C (i.e., a
diffraction pattern having two or more spots observed in a
selected area electron diffraction pattern), whereas the term
"amorphous region" used herein means a region characterized
20   by a diffraction pattern of, for example, a difficult-to-
graphitize carbon treated at 1,200 to 2,800°C (i.e., a
diffraction pattern having only one spot attributed to a
(002) plane observed in a selected area electron diffraction
pattern).

25   In the present invention, it is preferable that in a
bright field image observed under a transmission microscope,
an area ratio of a crystalline carbon portion to an amorphous
carbon portion in the carbonaceous particles be 95 to 50 : 5
to 50, more preferably 90 to 50 : 10 to 50. When the area
30   ratio of a crystalline carbon portion to an amorphous carbon
portion is less than 50 : 50, a negative electrode material

produced from the particles fails to attain high discharge
capacity. When the area ratio of a crystalline carbon
portion to an amorphous carbon portion is more than 95 : 5,
coulombic efficiency and cycle characteristics are
5   deteriorated due to the crystalline carbon portion
predominantly contained in the carbonaceous material, unless
the surface is completely covered with a carbon layer.
However, when the surface is completely covered with a carbon
layer, capacity decreases due to a problem intrinsic to a
10   double layer.

    [Compounded carbon powder material]
        In the present invention, a carbon material is
compounded with carbonaceous particles serving as a core
material. No particular limitation is imposed on the carbon
15   material. Examples of the carbon material include thermally
treated products of pitch, coke, and thermally treated
products of organic substance. The compounded carbon powder
material is preferably produced through a step of
incorporating an organic compound or a solution thereof into
20   core material particles through deposition and/or permeation,
and a step of carbonizing and/or graphitizing the organic
compound.
        The organic compound to be incorporated into the core
material particles through deposition and/or permeation in
25   the present invention is preferably a polymer capable of
bonding to the core material particles. The term "polymer
having a bonding property" refers to a substance which allows
core material particles to be tightly bonded together through
chemical bonding such as covalent bonding, van der Waals
30   bonding or hydrogen bonding or physical bonding such as an
anchor effect by intervening among the particles. Any

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polymer may be employed so long as the polymer exhibits a
resistivity against compression, bending, peeling, impact,
tension, tearing, etc. during treatment such as mixing,
stirring, removing of solvent, or heat treatment, to such a
5   degree that peel-off of the polymer from the particles is
virtually prevented. For example, the polymer is at least
one species selected from the group consisting of phenolic
resins, polyvinyl alcohol resins, furan resins, cellulose
resins, polystyrene resins, polyimide resins, and epoxy
10   resins. Of these, phenolic resins and polyvinyl alcohol
resins are preferred.

More preferably, the organic compound to be incorporated
into the carbonaceous particles serving as a core material
through deposition and/or permeation in the present invention
15   is a phenolic resin and/or starting materials therefor. A
dense carbonaceous material is produced by calcining a
phenolic resin. It is assumed that such a high density may
be realized through the process where unsaturated bonds of
starting materials for phenolic resin are reacted to form a
20   phenolic resin, which contributes to mitigating decomposition
during a heat treatment (or calcining) step, thereby
preventing foaming.

Among phenolic resins produced by reaction of a phenol
compound with an aldehyde compound, those employable in the
25   present invention are non-modified phenolic resins such as
novolak resins and resol resins and partially modified
phenolic resins. In addition, rubber such as nitrile rubber
may be added to the phenolic resin in accordance with needs.
Examples of the phenol serving as a starting material include
30   phenol, cresol, xylenol, and alkylphenols having an alkyl
group containing 20 or less carbon atoms.

17

The phenolic resin is preferably a so-called modified phenolic resin, which is produced by modifying a phenolic resin with a drying oil or a fatty acid thereof. Through incorporation of a drying oil or a fatty acid thereof,

5   foaming is further prevented during the calcination step, and thereby a carbonaceous layer of a higher density can be obtained.

The phenolic resin modified with a drying oil or a fatty acid thereof employable in the present invention may be

10   produced by causing a phenol compound to be addition-reacted with a drying oil in the presence of a strong acid catalyst, adding a base catalyst to the reaction mixture so as to adjust the conditions to be basic, and causing the mixture to be addition-reacted with formalin. Alternatively, the

15   modified phenolic resin may be produced by reacting a phenol with formalin, followed by adding a drying oil to the reaction product.

The drying oil is a vegetable oil which, when formed into thin film and exposed to air, is dried up and solidified

20   in a relatively short period of time. Examples of the drying oil include generally known oil species such as tung oil, linseed oil, dehydrated castor oil, soybean oil, and cashew nut oil, and a fatty acid contained in the oils.

The amount of the drying oil or a fatty acid thereof

25   with respect the phenolic resin is preferably 5 to 50 parts by mass based on 100 parts by mass of the phenolic resin (e.g., a phenol-folmalin condensate). When the amount of drying oil or fatty acid thereof is in excess of 50 parts by mass, bonding property of the core material particles of the

30   present invention decreases.

[Method for compounding carbon material]

18

The method of the present invention for compounding a carbon material with core material particles includes a step of incorporating an organic compound or a solution thereof into the core material particles through deposition and/or

5   permeation, and a step of carbonizing and/or graphitizing the organic compound. Alternatively, the method preferably includes a step of incorporating an organic compound or a solution thereof into the core material carbonaceous particles through deposition and/or permeation, a step of

10   heating the organic compound, and a step of carbonizing and/or graphitizing the organic compound. Through heat treatment of the organic compound or a solution thereof performed after incorporation thereof into the core material particles through deposition and/or permeation and before

15   carbonizing and/or graphitizing, the organic compound is tightly affixed, through polymerization or a similar process, to the carbonaceous particles.

No particular limitation is imposed on the amount of carbon material to be compounded, and the amount is

20   preferably 2 to 200 parts by mass based on 100 parts by mass of the carbonaceous particles, more preferably 4 to 100 parts by mass, most preferably 10 to 25 parts by mass.

In the present invention, the organic substance to be incorporated through deposition and/or permeation into the

25   core material particles is preferably a starting material for forming a polymer. This is because a starting material, which has a lower molecular weight/viscosity, can thoroughly and uniformly permeates into the inside of the core carbonaceous particles. As mentioned above, phenol resin is

30   preferred as a polymer, and thus starting materials for phenolic resins such as formalin and a phenolic derivative

19

are preferred.

Compounding phenolic resin with core material in liquid phase:

In the present invention, compounding a resin with core material particles is preferably performed through a method including reacting a phenol with a formaldehyde in the presence of a catalyst while mixing with the core material particles. The term "phenol" as used herein encompasses phenols as well as phenol derivatives. Besides phenol, phenol derivatives having three functional groups such as m-cresol and phenol derivatives having four functional groups such as bisphenol A are included. Alternatively, a mixture containing two or more of the aforementioned phenol derivatives may also be employed. Among formaldehydes, formalin is most preferred, but paraformaldehyde may also be employed. Examples of the reaction catalyst to be employed include a basic substance such as hexamethylenediamine, which forms an $-NCH_2$ bond between phenol and a benzene nucleus.

To a mixture containing a phenol compound, a formaldehyde and a reaction catalyst, core material particles are added, and the resultant mixture is allowed to react in a reaction vessel. In this case, the ratio by mole of phenol compound to formaldehyde is preferably set to be 1 (phenol compound) : a range of 1 to 3.5 (formaldehyde). The amount of the core material particles is preferably controlled to be within a range of 5 to 3,000 parts by mass based on 100 parts by mass of a phenol compound. The reaction is carried out in the presence of water in such an amount that the reaction system can be stirred.

Upon polymerization, reactant liquid must be caused to permeate cavities of core material particles. Accordingly,

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the reaction system may be evacuated once to ten-odd times before or during stirring. However, since a large amount of a phenol compound and a formaldehyde are vaporized in the process, it is preferable that the evacuation be carried out

5   after mixing the core material particles and water, and then after the pressure is adjusted to ambient pressure, a phenol compound and a formaldehyde are added and mixed therein. The lower the pressure in the vacuum, the more preferred, and a pressure of about 100 Torr to about 1 Torr is preferred.

10   Most of graphite powders employable as core material has a poor affinity to water. In such a case, graphite powder may be surface-oxidized in advance before use. Surface oxidation may be performed through any known method such as air oxidation, treatment by use of a nitric acid or a similar

15 compound, or treatment by use of an aqueous potassium bichromate solution.

When a phenol, a formaldehyde, a catalyst, core material particles and water are mixed, the reaction system at an initial stage has a mayonnaise-like viscosity. As time

20 elapses, a condensate of a phenol and a formaldehyde containing the core material particles begins to separate from water present in the system. At the time point when reaction reaches a desired reaction degree, stirring is terminated, and the mixture is cooled, whereby black

25 particles are precipitated. The precipitate is washed and filtered, to thereby provide compounded carbon particles employed in the present invention.

The amount of the precipitating resin can be elevated by increasing the concentration of phenol or formaldehyde in the

30 reaction system and can be lowered by decreasing the concentration of phenol or formaldehyde in the reaction

21

system. Thus, the amount of the precipitating resin can be controlled by modifying the amount of water, a phenol or a formaldehyde. The amount of water, a phenol, or a formaldehyde may be adjusted in advance before reaction, or

5   during reaction by adding dropwise any of these components into the reaction system.

The organic compound is preferably employed in the form of solution, since an organic compound can exhibit a lower viscosity in form of solution, which enables uniform and

10   complete permeation of the organic compound into the inside of the core material carbonaceous particles. No particular limitation is imposed on the solvent for preparing the solution, so long as a raw material for a polymer can be dissolved and/or dispersed in the solvent. Examples of the

15   solution include water, acetone, ethanol, acetonitrile, and ethyl acetate.

The atmosphere employed during deposition and/or permeation may be atmospheric pressure, elevated pressure, or reduced pressure. However, deposition is preferably carried

20   out under reduced pressure, since affinity of the carbon material particles to an organic compound increases.

Polymerization step may be carried out at a temperature of about 100 °C to about 500 °C.

The carbon material layer provided through deposition

25   and/or permeation according to the present invention is a highly crystalline carbon layer exhibiting a ratio of 0.4 or lower for a peak intensity at 1,360 cm^{-1} to a peak intensity at 1,580 cm^{-1} in a laser Raman spectrum. When the ratio is 0.4 or higher, the carbon layer has insufficient

30   crystallinity, thereby lowering the discharge capacity and coulombic efficiency of the battery electrode carbon material

of the present invention, which is not preferred.

[Method for depositing carbon fiber]

Preferably, carbon fiber is deposited on the surface of the carbon material for a battery electrode according to the present invention. Regarding the carbon fiber employed in the present invention, vapor grown carbon fiber produced through vapor phase growth is preferred, since the carbon fiber has high electrical conductivity, small fiber diameter, and high aspect ratio. Among vapor grown carbon fiber species, a vapor grown carbon fiber having high electrical conductivity and high crystallinity is preferred. When an electrode produced from the carbon material is incorporated in a lithium ion battery, current must be passed throughout the electrode (i.e., negative electrode) rapidly. Thus, preferably, vapor grown carbon fiber is grown in a direction parallel to the fiber axis and has a branched structure. When the carbon fiber has a branched structure, electric contact among carbon particles is facilitated by virtue of the branched fiber, thereby enhancing electrical conductivity.

The vapor grown carbon fiber may be produced through, for example, a method of feeding a gasified organic compound and iron serving as a catalyst into a high-temperature atmosphere.

Other than as-produced vapor grown carbon fiber, vapor grown carbon fiber which has been heat-treated at 800 to 1,500°C or which has been graphitized at 2,000 to 3,000°C may also be employed. Among them, vapor grown carbon fiber which has been treated at about 1,500°C is preferred.

In a preferred embodiment of the present invention, the vapor grown carbon fiber has a branched structure. The carbon filament, including branch portions, may have hollow

23

spaces in the inside, and a hollow space inside the filament
may communicate with hollow spaces in other portions of the
filament. In this case, tube-shaped carbon layers are
continuously linked together. The term "hollow structure"

5   refers to a tubular structure of a carbon layer and includes
an imperfect cylindrical structure, a cylinder having
partially cut off portions, and a carbon layer integrated
from two laminated carbon layers. No particular limitation
is imposed on the form of the cross-section of the cylinder,

10 the form may be a perfect circle, an oval or a polygon. No
particular limitation is imposed on the crystallinity of the
carbon layer, which is represented by the plane distance d_{002}.
The d_{002} as determined through X-ray diffraction is preferably
0.344 nm or less, more preferably 0.339 nm or less, most

15 preferably 0.338 nm or less, with Lc, the thickness of a
crystallite as measured along the c-axis, is 40 nm or less.

The vapor grown carbon fiber employed in the present
invention has a fiber outer diameter of 2 to 1,000 nm and an
aspect ratio of 10 to 15,000, preferably a fiber outer

20 diameter of 10 to 500 nm and a fiber length of 1 to 100 μm
(an aspect ratio of 2 to 2,000), or a fiber outer diameter of
2 to 50 nm and a fiber length of 0.5 to 50 μm (an aspect
ratio of 10 to 25,000).

After production of a vapor grown carbon fiber,

25 crystallinity of the fiber can be further increased through
heat treatment at 2,000°C or higher, thereby elevating the
electrical conductivity of the fiber. Before heat treatment,
addition of a substance such as boron, which enhances
graphitization degree, is effective for enhancing

30 crystallinity.

The vapor grown carbon fiber content of a negative

24

electrode is preferably 0.01 to 20 mass%, more preferably 0.1 to 15 mass%, most preferably 0.5 to 10 mass%. When the fiber content is in excess of 20 mass%, electric capacity is lowered. When the fiber content is less than 0.01 mass%,

5   internal resistance increases at low temperature (for example, -35°C).

The vapor grown carbon fiber has, on its surface, large amounts of irregularities and rough portions and exhibits enhanced adhesion to the carbonaceous particles serving as

10 core. Thus, even when charging/discharging cycles are repeated, the carbon fiber, which serves as a negative electrode active material and an electrical conductivity enhancer, can stay attached onto the carbonaceous powder particles and is not dissociated therefrom, whereby

15 electronic conductivity can be maintained and cycle characteristics are improved.

When the vapor grown carbon fiber contains a large amount of branched portions, conductive networks can be formed in an efficient manner, thereby readily attaining high

20 electronic conductivity and thermal conductivity. In addition, the carbon fiber can be dispersed in the active substance as if engulfing the particles of the active substance, thereby enhancing the strength of the resultant negative electrode and establishing favorable contact between

25 particles.

By virtue of vapor grown carbon fiber present among the active substance particles, retention of an electrolyte is enhanced, whereby lithium ions can be doped/undoped smoothly even at low temperature.

30 No particular limitation is imposed on the method for allowing carbon fiber to deposit onto a carbon material for a

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battery electrode of the present invention which is produced
by incorporating a carbon layer into carbonaceous particles
serving as core material through deposition and/or permeation.
For example, a carbon fiber having a fiber diameter of 2 to
5   1,000 nm can be deposited on carbonaceous particles by adding
the carbon fiber having a fiber diameter of 2 to 1,000 nm to
an organic compound (or a solution thereof) during a step of
allowing the organic compound (or a solution thereof) to
attach onto and/or permeate into the carbonaceous particles
10   serving as core material and bonding the carbon fiber to the
incorporated organic compound. Alternatively, in the present
invention, after depositing an organic substance on
carbonaceous particles serving as core material, a mixture of
particles including carbon fiber may be mixed into the carbon
15   material particles to deposit the carbon fiber on the
particles through stirring.

        No particular limitation is imposed on the stirring
method, and an apparatus such as a ribbon mixer, a screw
kneader, a Spartan ryuzer, a Lodige mixer, a planetary mixer,
20   or a general-purpose mixer may be employed.

        No particular limitation is imposed on the time and
temperature during the stirring process. These factors are
appropriately determined in accordance with the composition,
viscosity, and other properties of the particles and organic
25   substance. Generally, the temperature is about 0°C to about
150°C, preferably about 20°C to about 100°C.

        [Heat treatment conditions]

        In order to enhance charge/discharge capacity through
intercalation of lithium ions or other materials, enhancement
30   in crystallinity of the carbon material is required. Since
the crystallinity of carbon is generally enhanced in

accordance with the maximum point of thermal hysteresis, a
high heat treatment temperature is preferred for attaining an
enhanced battery performance.

5   The carbon material for a battery electrode according to
the present invention, in the case of using a graphite powder
as a core material which already has a high crystallinity,
does not particularly require a high-temperature heat
treatment. However, a heat treatment is required to some
extent for improving the crystallinity of a compounded carbon
10   layer. Specifically, such heat treatment is performed at
1,800 to 3,300°C, preferably 2,300°C or higher, more
preferably 2,500°C or higher, even more preferably 2,800°C or
higher, most preferably 3,000°C or higher. When the heat
treatment temperature is lower than 1,800°C, crystallinity
15   the compounded carbon layer obtains by the heat treatment is
insufficient, resulting in low discharge capacity and
deterioration of coulombic efficiency.

The temperature elevation rate for heat treatment does
not greatly affect the performance of the carbon material, so
20   long as it falls within a range of the maximum temperature
elevation rate and the minimum one employed in any known
apparatus. Since the carbon powder does not raise any
problems as would be experienced with molding material or
similar materials; e.g., cracking, a faster heating rate is
25   preferred from the viewpoint of costs. The time required to
reach the highest temperature from room temperature is
preferably 12 hours or shorter, more preferably 6 hours or
shorter, particularly preferably 2 hours or shorter.

Any known heating apparatus such as an Acheson furnace
30   or a direct heating furnace may be employed. Use of these
apparatus is advantageous from the viewpoints of costs.

27

However, nitrogen present in the apparatus may lower the resistance of the treated powder, and oxygen may reduce, through oxidation, the strength of the carbonaceous material. Therefore, it is preferable to use a furnace having such a

5   structure that the inside atmosphere can be maintained to be an inert gas such as argon or helium. Examples of such furnaces include a batch furnace which allows replacement of the inside atmosphere gas after completion of pressure reduction of a reactor, and a batch furnace and a continuous

10   furnace, in the form of a tubular furnace, which allows control of the atmosphere inside the furnace.

[Carbon material for battery electrode]

The carbon material for a battery electrode according to the present invention produced by compounding carbonaceous

15   particles serving as a core material with a carbon material preferably has a mean roundness (for the method of calculation, see the below-described Examples section) as measured by use of a flow particle image analyzer of 0.85 to 0.99. When the mean roundness is less than 0.85, the filling

20   density of the material during formation of an electrode cannot be elevated, thereby lowering the charge capacity per volume, whereas when the mean roundness is in excess of 0.99, it means that the material includes virtually no microparticles which have low roundness, thereby failing to

25   elevate the discharge capacity of the formed electrode. Furthermore, the amount of particles having a roundness less than 0.90 is preferably controlled to be within a range of 2 to 20% by number.

The carbon material for a battery electrode according

30   to the present invention produced by compounding carbonaceous particles serving as a core material with a carbon material

28

preferably has a mean particle size of 10 to 40 μm, more preferably 10 to 30 μm, as determined by laser diffraction.

When the mean particle size is too small, such carbonaceous particles do not effectively involved in

5   electrochemical reaction with lithium ions, thereby deteriorating capacity and cycle characteristics. Specifically, when the mean particles size is smaller than 1 μm, such particles tend to crack along a specific crystal direction during pulverization, thereby readily producing

10   particles of a high aspect ratio; i.e., increasing specific surface area. In the case of fabrication of a battery electrode, a negative electrode is generally produced by preparing a paste containing a negative electrode material with a binder and coating with the paste. When the mean

15   particle size of the negative electrode material is smaller than 10 μm, the material contains a considerably large amount of microparticles smaller than 1 μm, thereby elevating the viscosity of the paste, resulting in poor coatability.

When the mean particle size is 40 μm or larger, it means

20   that the material contains particles of 80 μm or larger, and the electrode surface becomes to have significant irregularities and rough portions, which may cause flaws on a separator employed in a battery. Thus, a carbon material containing virtually no particles of 1 μm or less and of 80

25   μm or more is preferably employed.

In the carbon material for a battery electrode according to the present invention, C_0 of a (002) plane as measured by means of X-ray diffractometry is preferably 0.6703 to 0.6800 nm, and the laser Raman R value preferably is 0.01 to 0.9.

30   Moreover, in a particle constituting the carbon material for a battery electrode according to the present invention, it is

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preferable that crystalline carbon portion and an amorphous
carbon portion be present dispersed, and the area ratio of
crystalline carbon portion to an amorphous carbon portion in
a bright field image observed under a transmission electron
5   microscope is 99 to 30 : 1 to 70, more preferably 95 to 70 :
5 to 30.

Particles constituting the carbon material for a battery
electrode according to the present invention may contain
boron. The amount of boron is preferably 10 to 5,000 ppm
10   based on the particle. By heat treatment at 1,800 to 3,300°C
in the presence of boron, graphitization of carbon can be
accelerated. Boron may be present in either or both of the
core material and the carbon layer present on the surface of
the core material. In a case of allowing boron to be
15   contained in the surface carbon layer, boron can be
incorporated into the carbon layer after polymerization of
organic compound, by adding boron or a boron compound before
heat treatment. Examples of boron compound include boron
carbide (B_4C), boron oxide (B_2O_3), boron in the elemental
20   state, boric acid (H_3BO_3) and borate.

[Fabrication of secondary battery]

By use of the carbon material for a battery electrode
according to the present invention produced by compounding
graphite particles serving as a core material with a carbon
25   material, a lithium ion battery can be fabricated through a
known method.

A lithium battery electrode is preferably formed from a
carbon material having a small specific surface area. The
carbon material of the present invention preferably has a
30   specific surface area of 0.2 to 5 m^2/g, more preferably 0.2
to 3 m^2/g, as measured through a BET method. When the

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specific surface area exceeds 5 m^2/g, surface activity of the
carbon material increases, and coulombic efficiency is
lowered as a result of, for example, decomposition of an
electrolytic solution. In order to increase capacity of a

5   battery, the filling density of the carbon material must be
increased. In order to increase the filling density, the
closer to spherical shape the shape of the carbon material
particle, the more preferable. When the shape of each
particle of the carbon material is represented by aspect

10   ratio (i.e., the length of the major axis/the length of the
minor axis), the aspect ratio is 6 or less, preferably 5 or
less. The aspect ratio may be obtained by use of, for
example, a micrograph of the carbon material. Alternatively,
the aspect ratio may be calculated through the following

15   procedure: the mean particle size (A) of the carbon material
is measured through a laser diffraction-scattering method;
the mean particle size (B) of the carbon material is measured
through an electrical detection method (a Coulter counter
method); each particle of the carbon material is regarded as

20   a disk, with the bottom diameter of the disk being
represented by (A); the volume (C) of the disk is calculated
from the formula: $C = 4/3 \times (B/2)^3\pi$; the thickness (T) of the
disk is calculated from the formula: $T = C/(A/2)^2\pi$; and
therefore the aspect ratio is calculated as A/T.

25   When a lithium battery electrode is formed from a carbon
material exhibiting good fillability and having high bulk
density, the electrode exhibits high discharge capacity per
volume.

     A battery electrode may be generally produced by

30   diluting a binder with a solvent, kneading the diluted binder
with a negative electrode material, and applying the mixture

to a collector (substrate).

Any known binders may be used in the present invention. Examples include fluorine-containing polymers such as polyvinylidene fluoride and polytetrafluoroethylene, and

5   rubbers such as SBR (styrene-butadiene rubber). Any known solvent suitable for the binder used may be employed. For example, when a fluorine-containing polymer is employed as a binder, toluene or N-methylpyrrolidone may be employed as a solvent, and when SBR is employed as a binder, water may be

10   employed as a solvent.

The amount of binder to be employed depends on the type of the binder and thus cannot be simply specified. In the case where such a fluorine-containing polymer is employed as a binder, the amount is preferably 5 to 20 parts by mass, on

15   the basis of 100 parts by mass of a negative electrode material. In the case where SBR is employed as a binder, the amount is preferably 1 to 10 parts by mass, more preferably about 1.5 to 5 parts by mass, on the basis of 100 parts by mass of a negative electrode material.

20   Kneading of the binder with the battery electrode carbon material of the present invention produced by incorporating a carbon layer into a substrate through deposition and/or permeation may be carried out by use of any known apparatus such as a ribbon mixer, a screw kneader, a Spartan ryuzer, a

25   Lodige mixer, a planetary mixer, or a general-purpose mixer.

In the present invention, a molded product prepared by pressing a mixture of the carbon material for a battery electrode and a binder at a pressure of 10^3 kg/cm^2 or higher has an intensity ratio of 0.1 or more, preferably 0.12 or

30   more, more preferably 0.15 or more, for peak intensity attributed to a (110) plane to peak intensity attributed to a

32

(004) plane determined through X-ray diffraction spectroscopic analysis. With such an peak intensity ratio, a material for a battery electrode, having excellent coulombic efficiency, cycle characteristics and high current

5   characteristics, involving little deformation and orientation due to pressurization, not deteriorating high discharge capacity of high crystalline graphite particles, and having a small irreversible capacity, can be obtained. When the peak intensity ratio of the intensity attributed to a (110) plane

10   to that attributed to a (004) plane is 1, it represents no orientation while the ratio is 0, it represents a 100% orientated state.

     Application of the kneaded mixture to a collector may be carried out through a known method. For example, the mixture

15   is applied to the collector by use of a doctor blade, a bar coater, or a similar apparatus, and then the resultant collector is subjected to molding through, for example, roll pressing.

     Examples of the material of the collector which may be

20   employed in the present invention include known materials such as copper, aluminum, stainless steel, nickel, and alloys thereof.

     Any known separator may be employed, but polyethylene- or polypropylene-made microporous film having a thickness of

25   5 to 50 μm is particularly preferred.

     In the lithium ion battery of the present invention, the electrolytic solution may be any known organic electrolytic solution, and the electrolyte may be any known inorganic solid electrolyte or polymer solid electrolyte. From the

30   viewpoint of conductivity, an organic electrolytic solution is preferred.

Examples of preferred organic solvents employable for preparing the organic electrolytic solution include ethers such as diethyl ether, dibutyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene

5   glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, diethylene glycol dimethyl ether and ethylene glycol phenyl ether; amides such as formamide, N-methylformamide, N,N-dimethylformamide, N-ethylformamide,

10 N,N-diethylformamide, N-methylacetamide, N,N-dimethylacetamide, N-ethylacetamide, N,N-diethylacetamide, N,N-dimethylpropionamide and hexamethylphosphoryl amide; sulfur-containing compounds such as dimethyl sulfoxide and sulfolane; dialkyl ketones such as methyl ethyl ketone and

15 methyl isobutyl ketone; cyclic ethers such as ethylene oxide, propylene oxide, tetrahydrofuran, 2-methoxytetrahydrofuran, 1,2-dimethoxyethane, and 1,3-dioxolan; carbonates such as ethylene carbonate and propylene carbonate; γ-butyrolactone; N-methylpyrrolidone; acetonitrile; and nitromethane. More

20 preferred examples include esters such as ethylene carbonate, butylene carbonate, diethyl carbonate, dimethyl carbonate, propylene carbonate, vinylene carbonate and γ-butyrolactone; ethers such as dioxolan, diethyl ether and diethoxyethane; dimethyl sulfoxide; acetonitrile; and tetrahydrofuran.

25 Particularly, carbonate-based non-aqueous solvents such as ethylene carbonate and propylene carbonate are preferably employed. These solvents may be employed singly or in combination of two or more species.

A lithium salt is employed as a solute (electrolyte)

30 which is to be dissolved in the aforementioned solvent. Examples of generally known lithium salts include $LiClO_4$,

34

$LiBF_4$, $LiPF_6$, $LiAlCl_4$, $LiSbF_6$, $LiSCN$, $LiCl$, $LiCF_3SO_3$, $LiCF_3CO_2$, $LiN(CF_3SO_2)_2$, and $LiN(C_2F_5SO_2)_2$.

Examples of the polymer solid electrolyte include polyethylene oxide derivatives and polymers containing the
5   derivatives, polypropylene oxide derivatives and polymers containing the derivatives, phosphoric acid ester polymers, and polycarbonate derivatives and polymers containing the derivatives.

In a lithium ion battery which employs the negative
10   electrode material of the present invention, a lithium-containing transition metal oxide is employed as a positive electrode material. The lithium-containing transition metal oxide is preferably an oxide predominantly containing lithium and at least one transition metal selected from among Ti, V,
15   Cr, Mn, Fe, Co, Ni, Mo and W, in which the ratio by mol between lithium and the transition metal is from 0.3 to 2.2. More preferably, the positive electrode active substance is an oxide predominantly containing lithium and at least one transition metal selected from among V, Cr, Mn, Fe, Co, and
20   Ni, in which the ratio by mol between lithium and the transition metal is from 0.3 to 2.2. The positive electrode active substance may contain Al, Ga, In, Ge, Sn, Pb, Sb, Bi, Si, P, B, etc. in an amount of less than 30 mol% on the basis of the entirety of the transition metal serving as a primary
25   component. Among the aforementioned positive electrode active substances, a preferred substance is at least one species selected from among materials being represented by the formula Li_xMO_2 (wherein M represents at least one element selected from among Co, Ni, Fe, and Mn, and x is 0 to 1.2);
30   or at least one species selected from among materials having a spinel structure and being represented by the formula

35

$Li_yN_2O_4$ (wherein N includes at least Mn, and y is 0 to 2).

Particularly preferably, the positive electrode active substance is at least one species selected from among materials containing $Li_yM_aD_{1-a}O_2$ (wherein M represents at least

5   one element selected from among Co, Ni, Fe and Mn; D represents at least one element selected from among Co, Ni, Fe, Mn, Al, Zn, Cu, Mo, Ag, W, Ga, In, Sn, Pb, Sb, Sr, B and P, with the proviso that the element corresponding to M being excluded; y is 0 to 1.2; and a is 0.5 to 1); or at least one

10 species selected from among materials having a spinel structure and being represented by the formula $Li_z(N_bE_{1-b})_2O_4$ (wherein N represents Mn; E represents at least one element selected from among Co, Ni, Fe, Mn, Al, Zn, Cu, Mo, Ag, W, Ga, In, Sn, Pb, Sb, Sr, B, and P; b is 1 to 0.2; and z is 0 to 2).

15   Specific examples of the positive electrode active substance include Li_xCoO_2, Li_xNiO_2, Li_xMnO_2, $Li_xCo_aNi_{1-a}O_2$, $Li_xCo_bV_{1-b}O_z$, $Li_xCo_bFe_{1-b}O_2$, $Li_xMn_2O_4$, $Li_xMn_cCo_{2-c}O_4$, $Li_xMn_cNi_{2-c}O_4$, $Li_xMn_cV_{2-c}O_4$, and $Li_xMn_cFe_{2-c}O_4$ (wherein x is 0.02 to 1.2, a is 0.1 to 0.9, b is 0.8 to 0.98, c is 1.6 to 1.96, and z is 2.01

20 to 2.3). Examples of most preferred lithium-containing transition metal oxides include Li_xCoO_2, Li_xNiO_2, Li_xMnO_2, $Li_xCo_aNi_{1-a}O_2$, $Li_xMn_2O_4$ and $Li_xCo_bV_{1-b}O_z$ (wherein x is 0.02 to 1.2, a is 0.1 to 0.9, b is 0.9 to 0.98, and z is 2.01 to 2.3). The value x is a value as measured before initiation of

25 charging/discharging, and is increased or decreased through charging/discharging.

No particular limitation is imposed on the mean particle size of particles of the positive electrode active substance, but the mean particle size is preferably 0.1 to 50 μm.

30 Preferably, the volume of particles having a particle size of 0.5 to 30 μm is 95% or more on the basis of the entire volume

of the positive electrode active substance particles. More
preferably, the volume of particles having a particle size of
3 μm or less is 18% or less on the basis of the entire volume
of the positive electrode active substance particles, and the
5   volume of particles having a particle size of 15 μm to 25 μm
inclusive is 18% or less on the basis of the entire volume of
the positive electrode active substance particles. No
particular limitation is imposed on the specific surface area
of the positive electrode active substance, but the specific
10 surface area as measured by means of the BET method is
preferably 0.01 to 50 m^2/g, particularly preferably 0.2 m^2/g
to 1 m^2/g. The supernatant formed when the positive electrode
active substance (5 g) is dissolved in distilled water (100
ml) preferably has a pH of 7 to 12.
15   No particular limitation is imposed on the selection of
elements required for producing a battery, other than the
aforementioned elements.

EXAMPLES

20   The present invention will next be described in more
detail with reference to representative examples, which are
provided for illustration purposes only and should not be
construed as limiting the invention thereto.
Method for measuring orientation characteristics of powder
25 and electrode sheet through X-ray diffraction:
        The electrode which had been subjected to pressing at a
predetermined pressure was affixed to a measurement cell by
use of double-faced adhesive tape. The measurement cell was
then placed in an X-ray diffraction apparatus employing the
30 following conditions:
        Conditions for X-ray generation: voltage 40 kV and

current 30 mA;

Measurement range: 74 to 80° ((110) plane) and 52 to 58° ((004) plane); and

Tube: copper.

5   The obtained waveforms were smoothed, and the background intensity and the $K\alpha_2$ peak were subtracted. For each waveform, the peak intensity ratio was calculated from the maximum peak intensity at $2\theta = 77$ to 78.5° for the (110) plane and the maximum peak intensity at $2\theta = 53.2$ to 54.7° for the (004)

10   plane.

Method for measuring the mean roundness:

The mean roundness of the carbon material according to the present invention was measured by use of a flow particle image analyzer FPIA-2100 (product of Sysmex Corporation), as

15   described below.

A measurement sample was subjected to cleaning (removal of micro dust) by use of a 106 μm filter. The sample (0.1 g) was added to ion-exchange water (20 mL), and an anionic/nonionic surfactant (0.1 to 0.5 mass%) was added to

20   the resultant mixture so as to uniformly disperse the sample in the mixture. Dispersion of the sample was carried out for five minutes by use of ultrasonic cleaner UT-105S (product of Sharp Manufacturing Systems Corporation), thereby preparing a measurement dispersion containing the sample. The summary of

25   measurement principle and other details are provided in, for example, "*Funtai to Kogyo*," VOL. 32, No. 2, 2000, and Japanese Patent Application Laid-Open (Kokai) No. 8-136439 (U.S. Patent No.5721433). Specifically, the measurement will further be described as follows.

30   When the measurement sample dispersion passes through the flow path of a flat, transparent flow cell (thickness:

about 200 μm), the dispersion is irradiated with strobe light

at intervals of 1/30 second, and photographed by a CCD camera.

A predetermined number of still images were captured and

image analysis was performed on the images, followed by

5   calculation according to the following formula.

Roundness = (the circumference of a circle as calculated

from a circle-equivalent diameter)/(the perimeter of a

projected image of a particle)

The term "circle-equivalent diameter" refers to the

10   diameter of a true circle having an area equal to the actual

projection area of a particle that has been obtained from a

photograph of the particle. The roundness of the particle is

obtained by dividing the circumference of a circle as

calculated based on the circle-equivalent diameter by the

15   actual perimeter of the projected particle. For example, a

particle having a true round shape has a roundness of 1,

whereas a particle having a more complicated shape has a

roundness of a smaller value.

The mean roundness of particles is the averaged

20   roundness value for each of the measured particles as

obtained by means of the above-described method.

Method for measuring the average particle size:

The measurement was carried out by using a laser

scattering particle size distribution analyzer, Microtrac

25   HRA (product of NIKKISO Co., Ltd.). A sample (0.05 g) was

placed in a 200ml beaker, two drops of a 0.1 % aqueous

solution of Triton X-100 (manufactured by ICN Biochemicals,

INC, distributed by Wako Pure Chemical Industries, Ltd.) were

added thereto, further, 500 ml of purified water was added

30   thereto, the resultant mixture was subjected to ultrasonic

dispersion for 5 minutes, and then the measurement was carried out on the sample.

Battery evaluation method:

(1) Preparation of paste for forming electrode sheet:

5   Negative electrode material (9.7 g), carboxymethyl cellulose (CMC) (HB-45, product of ZEON Corporation) as a solid (1.5g) and SBR (BM-400B, product of ZEON Corporation) as a solid (1.5g) were mixed, and further, purified water was added thereto so that the total water content in the

10   resultant mixture was 6.9 g. With a 12ϕ-Teflon™ ball, the mixture was kneaded by using a defoaming kneader (NBK-1:manufactured by Nippon Seiki Co., Ltd.) at 500 rpm for 5 minutes, to thereby prepare a stock liquid.

(2) Formation of electrode sheet:

15   By use of a doctor blade, the obtained stock liquid was applied onto a sheet of high purity copper foil so as to attain a thickness of 250 μm. The thus-obtained product was dried under vacuum at 120°C for one hour, and then subjected to punching, to thereby form an electrode having a size of 18

20   mmϕ. The thus-formed electrode was sandwiched between pressing plates made of super steel, and then subjected to pressing such that a pressure of 0.5×10^3 to 0.7×10^3 kg/cm^2 was applied to the electrode.

Thereafter, the resultant electrode was dried in a

25   vacuum drying apparatus at 120°C for 12 hours, and then employed for evaluation.

The above electrode was also used in the aforementioned measurement on orientation characteristics of electrode sheet through X-ray diffraction.

30   (3) Fabrication of battery

A three-electrode cell was produced as follows. The

below-described procedures were carried out in an atmosphere of dried argon having a dew point of -80°C or lower.

In a polypropylene-made cell (inner diameter: about 18 mm) having a screw cap, a separator (polypropylene-made microporous film (Celgard 2400)) was sandwiched between the copper-foil-coated carbon electrode (positive electrode) formed in above (2) and a metallic lithium foil (negative electrode), to thereby form a laminate. Subsequently, a metallic lithium foil serving as a reference electrode was laminated in a manner similar to that described above. Thereafter, an electrolytic solution was added to the cell, and the resultant cell was employed for testing.

(4) Electrolytic solution

EC system: The electrolytic solution was prepared by dissolving $LiPF_6$ (1 mol/liter) serving as an electrolyte, in a mixture of EC (ethylene carbonate) (8 parts by mass) and DEC (diethyl carbonate) (12 parts by mass).

(5) Charging/discharging cycle test

Constant-current constant-voltage charging/discharging test was performed at a current density of 0.2 mA/cm^2 (corresponding to 0.1 C).

Constant-current (CC) charging (lithium charging to carbon) was performed at 0.2 mA/cm^2 while voltage was increased from rest potential to 0.002 V. When the voltage reached 0.002 V, the charger was switched over to constant-voltage (CV). Subsequently, the charging was performed at 0.002 V, and was stopped when the current value decreased to 25.4 μA.

CC discharging (lithium discharging from carbon) was performed at 0.2 mA/cm^2 (corresponding to 0.1 C), and was cut off when a voltage of 1.5 V was attained.

41

Example 1:

    As a graphite material serving as core material, there
was employed carbonaceous powder (100 g) having a laser

5   diffraction mean particle size of 20 μm, a mean roundness of
0.88, and an area ratio of 80:20 for crystalline carbon-
portion/amorphous carbon portion as determined in a bright
field image observed under a transmission electron microscope.
The graphite material had a BET specific surface area of 5.6

10   m^2/g, and a C$_0$ of 0.6710 nm, as measured through X-ray
diffraction spectroscopy. By a laser Raman spectrum of the
surface of the graphite material, the peak intensity ratio
for the peak intensity at 1,360 cm^{-1} /the peak intensity at
1,580 cm^{-1} was 0.21.

15   The graphite material (300 parts by mass), phenol (398
parts by mass), 37% formalin (466 parts by mass),
hexamethylenetetramine (38 parts by mass) serving as a
reaction catalyst, and water (385 parts by mass) were fed
into a reaction container. The mixture was stirred at 60 rpm

20   for 20 minutes. Air was evacuated from the reaction
container to 3 Torr while stirring was continued, the mixture
was maintained in vacuum for 5 minutes, and then the pressure
was recovered to atmospheric pressure. This procedure was
repeated three times under continuous stirring, to thereby

25   cause the solution to permeate deeply into granulated
products. Stirring was further continued, while the mixture
was heated and maintained at 150°C. The mixture initially had
mayonnaise-like fluidity, but gradually, a reaction product
of phenol and formaldehyde containing graphite began to

30   separate from a layer predominantly containing water. After
about 15 minutes, black particles composed of graphite and

phenolic resin began to be dispersed in the reaction
container. Subsequently, stirring was further continued at
150°C for 60 minutes, the contents of the reactor were cooled
to 30°C, and stirring was stopped. Black particles obtained
5 through filtration of the contents of the reactor were washed
with water, filtered again, and then subjected to a drying
process employing a fluidized-bed dryer. The particles were
dried under 55°C hot air for 5 hours, whereby particles of
graphite/phenolic resin were obtained.

10   The thus-obtained graphite/phenolic resin particulate
product was pulverized with a Henschel mixer at 1,800 rpm for
5 minutes. The pulverized mixture was placed in a heating
furnace, and air in the furnace was evacuated, followed by
changing the atmosphere to argon. The mixture was heated to
15 3,000°C under argon flow and maintained at this temperature
for 10 minutes. Subsequently, the mixture was cooled to room
temperature. The thus-obtained product was sieved by use of
a sieve having openings of 63 μm. The undersized product was
employed as a negative electrode material sample. The
20 selected area electron diffraction pattern was analyzed for
square regions (5 μm × 5 μm) arbitrary selected from a
transmission electron microscope image (× 25,000) of the
sample. The analysis revealed that the area ratio of a
region having two or more spots to a region having a single
25 spot attributed to the (002) plane in the diffraction pattern
was found to be 82 : 18. C_0 measured through X-ray
diffraction spectroscopy was found to be 0.6715 nm. By a
laser Raman spectrum of the surface of the graphite material,
the peak intensity ratio for the peak intensity at 1,360 cm^{-1}
30 /the peak intensity at 1,580 cm^{-1} was found to be 0.20. The
results indicate that the negative electrode material sample

43

had high crystallinity similar to that of the graphite
material serving as core material. These compounded graphite
particles were found to have a mean particle size of 15 µm, a
mean roundness of 0.92 and a specific surface area of 1.5

5 m^2/g. The amount of carbon layer derived from phenolic resin
was 50.8 parts by mass based on 100 parts by mass of the core
material graphite particles.

By use of the compounded graphite particles, an
electrode sheet samples were formed through the

10 aforementioned method. Table 1 shows the orientation
characteristics of the powders and the electrode sheets, as
determined through X-ray diffraction. Each electrode sheet
was placed in a battery testing apparatus using a single cell
and the EC system serving as an electrolyte for a cell test.

15   The testing apparatus was used to measure capacity and
coulombic efficiency after the first cycle of a
charging/discharging test and capacity after 50 test cycles.
The results are shown in Table 2.

20 Example 2:
As a graphite material serving as a core material, there
was employed a carbonaceous powder (100 g) prepared by
processing flake graphite material having a mean particle
size of 5 µm with a hybridizer (product of Nara Machinery Co.,

25 Ltd.) for rounding the particles, and having a laser
diffraction mean particle size of 15 µm, a mean roundness of
0.86, and an area ratio of 90:10 for crystalline carbon-
portion/amorphous carbon portion as determined in a bright
field image observed under a transmission electron microscope.

30 The graphite particles had a BET specific surface area of 5.3
m^2/g, and a C$_0$ of 0.6712 nm, as measured through X-ray

44

diffraction spectroscopy. By a laser Raman spectrum of the surface of the graphite material, the peak intensity ratio for the peak intensity at 1,360 cm^{-1} /the peak intensity at 1,580 cm^{-1} was found to be 0.20. The graphite powder was

5   further treated in a manner similar to that of Example 1.

The orientation characteristics of the powders and the electrode sheets were determined through X-ray diffraction. Fig. 1 shows an X-ray diffraction pattern of an electrode sheet at the (004) plane, and Fig. 2 shows an X-ray

10   diffraction pattern of an electrode sheet at the (110) plane. The maximum peak intensity ratios are shown in Table 1.

The testing apparatus was used to measure capacity and coulombic efficiency after the first cycle of a charging/discharging test and capacity after 50 test cycles.

15   The results are shown in Table 2.

Example 3:

As a graphite material serving as a core material, there was employed a carbonaceous powder (100 g) that had a laser

20   diffraction mean particle size of 15 μm, a mean roundness of 0.88, and an area ratio 80 : 20 for crystalline carbon portion/amorphous portion as determined in a bright field image observed under a transmission electron microscope. The graphite particles had a BET specific surface area of 5.6

25   m^2/g, and a C$_0$ of 0.6716 nm, as measured through X-ray diffraction spectroscopy. By a laser Raman spectrum of the surface of the graphite material, the peak intensity ratio for the peak intensity at 1,360 cm^{-1} /the peak intensity at 1,580 cm^{-1} was found to be 0.22.

30   An ethanol solution of phenolic resin monomers (55 parts by mass in terms of resin solid) and ethanol (50 parts by

mass) were mixed and stirred until the monomers were completely dissolved in water. The thus-obtained solution was added to the aforementioned carbonaceous powder so that the phenolic resin solid content was adjusted to 20 mass%

5 with respect to the carbonaceous powder. The mixture was kneaded for 30 minutes by use of a planetary mixer. The kneaded mixture was dried in a dryer under reduced pressure at 150°C for 2 hours. Subsequently, the mixture was placed in a heating furnace, and air was evacuated from the furnace,

10 followed by changing the atmosphere to argon. The mixture was heated to 3,000°C under argon flow and maintained at this temperature for 10 minutes. Subsequently, the mixture was cooled to room temperature. The thus-obtained product was sieved by use of a sieve having openings of 63 μm. The

15 undersized product was employed as a negative electrode material sample. Thus, the negative electrode material of Example 3 was produced. By a laser Raman spectrum of the surface of the graphite material, the peak intensity ratio for the peak intensity at 1,360 cm^{-1} /the peak intensity at

20 1,580 cm^{-1} was found to be 0.24. The negative electrode material sample was further treated in the same manner as in Example 1.

      Each electrode sheet was placed in a battery testing apparatus using a single cell and the EC system serving as an

25 electrolyte for a cell test.

      Table 1 shows the orientation characteristics of the powders and the electrode sheets, as determined through X-ray diffraction. The above testing apparatus was used to measure capacity and coulombic efficiency after the first cycle of a

30 charging/discharging test and capacity after 50 test cycles. The results are shown in Table 2.

Example 4:

Samples were prepared by the same manner as in Example 1 except that a vapor grown carbon fiber (5 mass%) (fiber
5   diameter: 150 nm, aspect ratio: 100) which had been graphitized at 2,800°C was added to and mixed with the content of the reaction container before reaction and then stirred. The orientation characteristics of the powders and the electrode sheets (shown in Table 1) were determined
10   through X-ray diffraction in the same manner as in Example 1. Each electrode sheet was placed in a battery testing apparatus using a single cell and the EC system serving as an electrolyte for a cell test. The testing apparatus was used to measure capacity and coulombic efficiency after the first
15   cycle of a charging/discharging test and capacity after 50 test cycles. The results are shown in Table 2.

Comparative Example 1:

A carbonaceous powder serving as a core material in
20   Example 1 (laser diffraction mean particle size : 20 μm, mean roundness: 0.88, and an area ratio of 80 : 20 for crystalline carbon portion/amorphous carbon portion as determined in a bright field image observed under a transmission electron microscope) was employed without coating the surface of the
25   material with carbon layer. By a laser Raman spectrum of the surface of the graphite material, the peak intensity ratio for the peak intensity at 1,360 cm^{-1} /the peak intensity at 1,580 cm^{-1} was found to be 0.39.

The orientation characteristics of the samples obtained
30   in Comparative Example 1 were determined through X-ray diffraction in the same manner as in Example 1. The X-ray

47

diffraction peak of an the electrode sheet at the (004) plane
is shown in Fig. 3, and the peak at the (110) plane is shown
in Fig. 4. The maximum peak intensity ratios are shown in
Table 1. Each electrode sheet was placed in a battery

5   testing apparatus using a single cell and the EC system
serving as an electrolyte for a cell test, and by use of the
testing apparatus, capacity and coulombic efficiency after
the first cycle of a charging/discharging test and capacity
after 50 test cycles were measured. The results are shown in

10   Table 2.

Comparative Example 2:
      The same materials and treatment as those of Example 1
were employed except that the final heat treatment was

15   performed at 1,000°C, to thereby prepare samples of
Comparative Example 2.
The selected area electron diffraction pattern was analyzed
for square regions (5 μm × 5 μm) arbitrary selected from a
cross-section TEM image of the sample. The analysis revealed

20   that the area ratio for a region having two or more spots to
a region having a single spot attributed to the (002) plane
in the diffraction pattern was found to be 25 : 75. Capacity
and coulombic efficiency after the first cycle of a
charging/discharging test and capacity after 50 test cycles

25   were measured. The results are shown in Table 2.

Table 1

Sample	Peak intensity ratio		
	No pressing (powder)	Pressed at 1 ton	Pressed at 3 tons
Example 1	0.45	0.13	0.12
Example 2	0.53	0.20	0.17
Example 3	0.59	0.28	0.19
Example 4	0.44	0.12	0.11
Comparative Example 1	0.17	0.037	0.032
Comparative Example 2	0.18	0.035	0.033

Table 2

Sample	Capacity (mAh/g) (1st Cycle)	Coulombic efficiency (%) (1st Cycle)	Capacity (mAh/g) (After 50 Cycles)
Example 1	360	94	356
Example 2	352	93	349
Example 3	350	92	345
Example 4	353	93	352
Comparative Example 1	330	90	325
Comparative Example 2	350	89	310

5

INDUSTRIAL APPLICABILITY

According to the present invention, a carbon material having high discharge capacity and small irreversible capacity and exhibiting excellent coulombic efficiency and
10   cycle characteristics, which is useful as a lithium ion secondary battery negative electrode material, can be

screened by use of X-ray parameter which shows the carbon
particle orientation of the produced electrode. The method
for producing a carbon material of the present invention has
excellent cost-effectiveness and mass productivity, employs a
5   coating material easy to handle, and is an improved method
which ensures safety.

When the battery electrode material according to the
present invention is employed for producing a battery, the
battery attains a discharge capacity of 340 mAh/g or more,
10   specifically 340 to 365 mAh/g.